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Pressure carbonization of pitch/phenolic resin mixtures

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Phenolic resins and the benzene-soluble fraction of a coal tar pitch were mixed in a solvent (pyridine) and carbonized at 600° C in a gold tube under a pressure of 30 MPa. Yields, optical textures and graphitizabilities of the carbons were studied. Large carbon yields (> 80%) were obtained from sealed tubes under pressure (closed system). In open tubes under pressure (open system), only slight improvements in carbon yields were observed. As the resin content in the starting mixtures increased, the optical texture of the resultant carbons decreased from coarse mosaic to isotropic through intermediates with a gradual decrease in size of mosaic units. These intermediate optical textures occurred with a wider range of resin content under pressure than under atmospheric pressure, especially from closed systems. Changes in structural parameters of the carbons after the 2800° C treatment corresponded to the changes in optical texture with resin content.

1. Introduction

In the manufacture of carbon fibre/carbon composites, pitch is the precursor of matrix carbon [1, 2], because of little carbonization shrinkage and few pyrolysis cracks in the matrix carbon unlike that derived from thermosetting resins. With pitch, preferred orientation of the basal planes of the matrix carbon is created during carbonization of the composites [3]. The structure of matrix carbon, which can be seen under the polarized light microscope as an optical texture, considerably affects the properties of the resultant composites, such as thermal conductivity, electrical conductivity and mechanical properties [4–6]. To control the optical texture of carbons, the carbonization of pitch/phenolic resin systems has been studied. This shows that the average size of mosaics in the optical texture of the carbon decreases with increasing resin content in the starting mixtures [7, 8].

The conditions of carbonization also influence the optical texture of resultant carbons. Carbonization under pressure modifies the optical texture and gives high yields of carbon [9–11]. The latter is an advantage as it improves the density of the composites. Recently, Forrest and Marsh reported increases in carbon yield by the pressure carbonization of pitch/resin mixtures and changes in optical texture with mixing ratio and carbonization pressure [12]. Improvement in the interaction of pitch and resins by applied pressure was shown, resulting in optical homogeneous texture carbons. With large percentages of resin added, however, there was less complete interaction of pitch and resins, with the isolation of two phases of pitch carbon and resin carbon.

In a previous paper [7], at large percentages of added resin the homogeneous carbons could be obtained under atmospheric pressure, when the pitch and resin were mixed using a solvent. In the present work, the pitch/phenolic resin mixtures were carbonized under pressure using this method. The yield after carbonization, the optical texture and graphitizability of the carbon obtained were

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studied in order to ascertain the usefulness of carbonization in the control of optical texture and, consequently, to produce carbon/carbon composites.

2. Experimental procedure

The benzene-soluble fraction of a coal tar pitch and two types of phenolic resin, resol- and novolac-type, were used as the starting materials. The resol-type resin contains about 30 vol % ethylene glycol. With various ratios the pitch and resin were dissolved and mixed completely in minimal amounts of pyridine. After removing the pyridine, the mixtures were cured at 120° C for 5 h in air and then post-cured at 200° C for 5 h in nitrogen. The details of the starting materials and the solvent-mixing technique were reported previously [7].

The post-cured samples were sealed in thin-walled gold tubes of 7 mm diameter (closed system), Before sealing, the air in the tube was replaced with argon. Using an autoclave, the sealed gold tube was heated to 650° C under a nitrogen pressure of 30 MPa and kept at 650° C for 5 h. The post-cured samples were also heated in the same way, without sealing the tube (open system). The carbon yield from the mixtures was determined from the change in weight between post-cured and carbonized samples. The optical texture of carbonized samples was examined on a polished section under a polarized-light microscope.

The carbonized samples thus obtained were heated to 2800° C and kept for 30 min in an atmosphere of argon. The X-ray structural parameters were determined using nickel-filtered Cu$K\alpha$ radiation and silicon as a standard.

3. Results and discussion

3.1. Optical texture and carbon yield

After carbonization under the closed system, the carbon from pure pitch had the same shell shape as the inside wall of the tube. As resin content of the starting mixtures increased, the carbon at the bottom of the tube became thicker and could be differentiated from flaky carbon adhering to the inside wall of the tube. In resin contents up to 80% resol-type resin and up to 70% novolac-type resin, there were no appreciable differences in optical texture between the bottom carbon and flaky carbon. At higher contents of resin, however, heterogeneous optical textures were observed in the flaky carbons and their X-ray diffraction profiles after heat-treatment at 2800° C showed composite profiles consisting of a broad major peak and a weak but relatively sharp peak. In the open system, on the other hand, mostly bottom type carbon was obtained with almost no flaky carbon on the wall of the tube. In this study, the carbon obtained at the bottom of the tube was used in successive experiments, because the flaky carbon was formed with $< 20\%$ yield.

Polarized-light micrographs in Fig. 1 show the decrease in size of the optical texture of carbon with increasing resin content in the starting mixtures. The transition in optical texture is seen from coarse mosaic to isotropic carbon through intermediates, i.e. a gradual decrease in the size of mosaic units. Fig. 2 illustrates the changes in optical texture of the carbons as a function of resin content, in comparison with the results under normal pressure. Here the optical textures are described in terms of coarse mosaic, medium mosaic, fine mosaic and isotropic, corresponding to mosaic units sizes of > 100, 100 to 10, $< 10\,\mu$m and optically inactive, respectively. Under pressure, the optical texture of the resultant carbons gradually changes over a range of resin content, the range being wider in the closed system under pressure than under normal pressure. In the open system, the transition range widens towards both sides of lower and higher resin content. In the closed system, on the other hand, the transition range seems to be wider towards higher resin content. The resol- and novolac-type resins produce the same effect on the optical texture of the resultant carbons, except for the amount of resin to produce a transition range. This difference, however, can be explained by the presence of $\sim 30\%$ ethylene glycol in the starting resol-type resin, as pointed out in our previous paper [8].

In Fig. 3 the carbon yield at 650° C is plotted against resin content in the starting mixtures. Under the closed system, a large carbon yield (more than 80%) is obtained, as expected. Carbonaceous materials, which would have volatilized out either under normal pressure or in the open system under pressure, are effectively converted to carbon residue in the closed system. In the open system under pressure, an increase in carbon yield from that under normal pressure is observed for mixtures with low resin content. Above 40% resin content, no appreciable increase is found. The increment in carbon yield on pressurization depends strongly on the number-average molecular weight of the

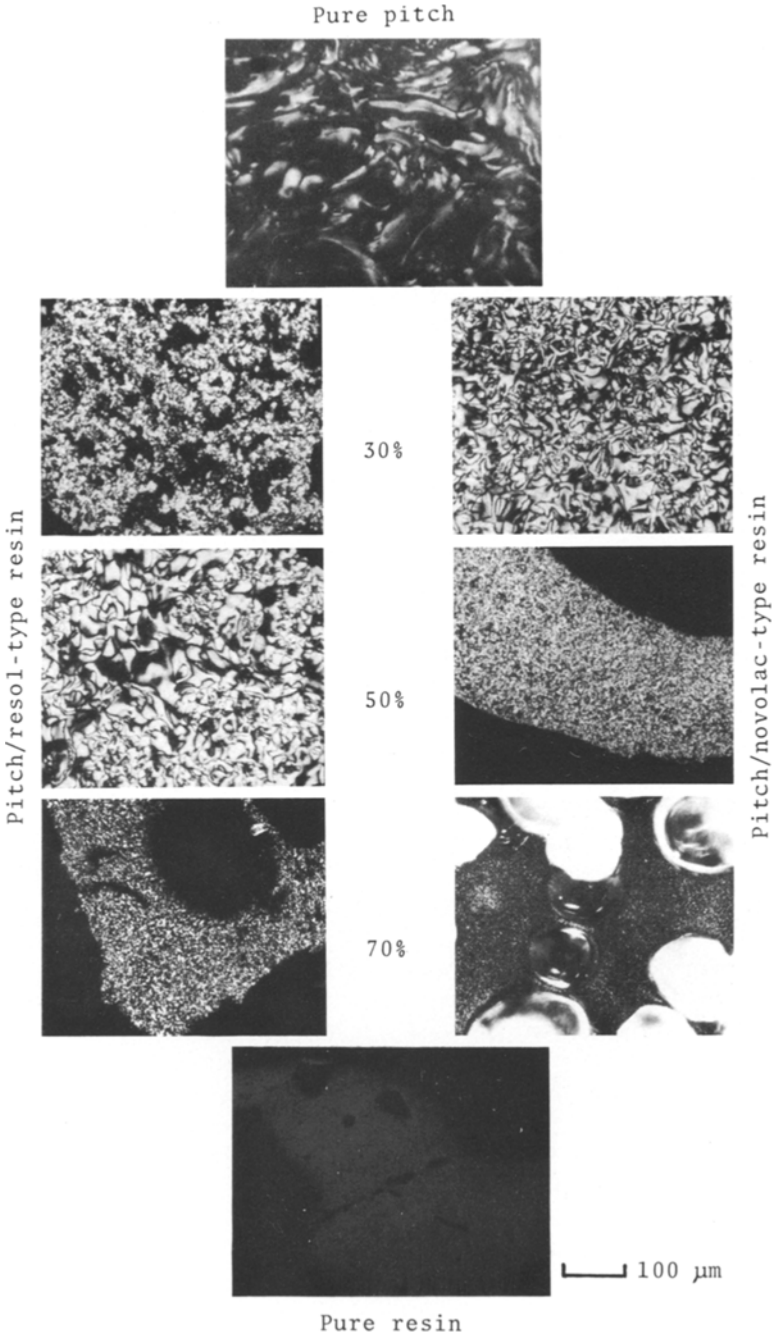

Figure 1 Polarized-light micrographs of polished sections of the carbons made from pitch/phenolic resin mixtures by carbonization in sealed gold tubes under a pressure of 30 MPa.

fractionated pitch: the larger the increment the lower the molecular weight fraction [11]. There is little difference in carbon yield between the mixtures with resol- and novolac-type resins. This is due to the fact that the carbon yield was calculated on the basis of the weight after post-curing where almost all the ethlene glycol in the resol-type resin vaporized out, as discussed previously [8].

3.2. Effect of pressure on optical texture

There are three effects of pressure:

1. the decrease in fluidity;

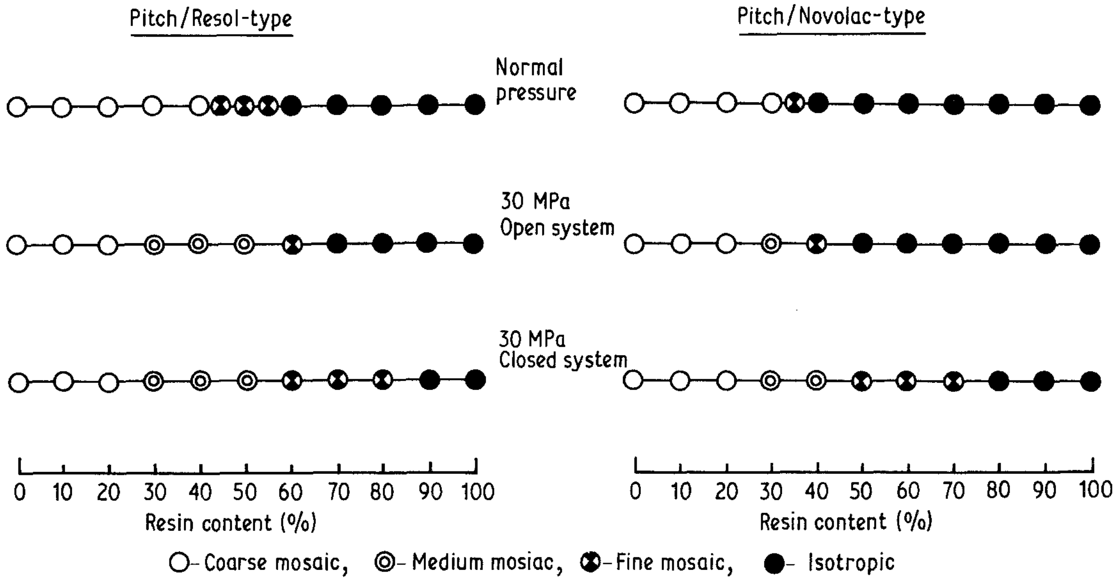

Figure 2 Variations in optical texture of the carbons with resin content in the starting pitch/phenolic resin mixtures.

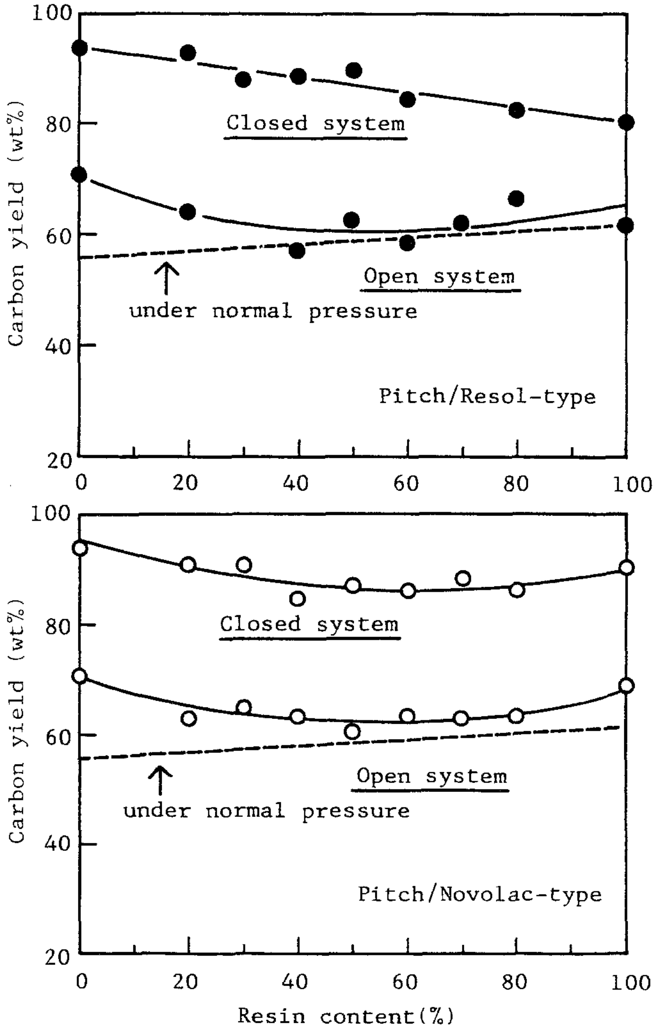

Figure 3 Relations between carbon yield and resin content in the starting mixtures after carbonization under a pressure of 30 MPa at 650° C. The broken line shows the relation under normal pressure [8].

2. the suppression of the loss of volatile matter of low molecular weight;

3. the retardation of the growth and coalescence of spheres of mesophase.

The first may be said to be a physical effect and the latter two chemical effects. These three relate to each other, for example, the effect 3 is caused at least partly from effect 1. Effects 1 and 3 are cooperative in reducing the size of mosaic units of the resultant carbons. However, effect 2 seems to be competitive with effects 1 and 3, because the incorporation of low molecular weight components, which would be lost as volatile matter under normal pressure, into the carbonization system, lowers the viscosity of the fluid state. In the pitch-rich mixtures, below 30% resin, the size of mosaic units in optical texture decreases from coarse mosaic under normal pressure to medium mosaic under pressure, probably because effects 1 and 3 overcome effect 2, though a large amount of low molecular weight components is retained. Above 60% resol- and 40% novolac-type resin, effect 2, that is the suppression of the loss of low molecular weight components, seems to work effectively with the increase in resin content, fine mosaic texture under normal pressure changing to medium mosaic under pressure and isotropic to fine mosaic. In the closed system, effect 2 influences the optical texture more than in the open system, because larger amounts of lower molecular weight components are retained, seen by the increase in carbon yield (Fig. 3).

3.3. Graphitizability

The graphitizability of the carbons obtained depended strongly on the resin content, as shown in Fig. 4, from X-ray diffraction profiles of the 2800° C-treated carbons. As the resin content in the starting mixture increases, the 002 profile gradually broadens and shifts to the lower angle side of diffraction. All the samples are expected to behave homogeneously during graphitization because all the profiles do not show detectable asymmetry. In Fig. 5 changes in X-ray structural parameters calculated from 002 and 110 diffractions are shown. With the increase in resin content in the starting mixtures, the average interlayer spacing, d_{002}, increases, and the crystallite thickness, $L_c(002)$, and crystallite diameter, L_a, decrease. The carbons prepared from mixtures with lower resin content have large values of $L_c(002)$ and L_a, beyond the scale of the figures.

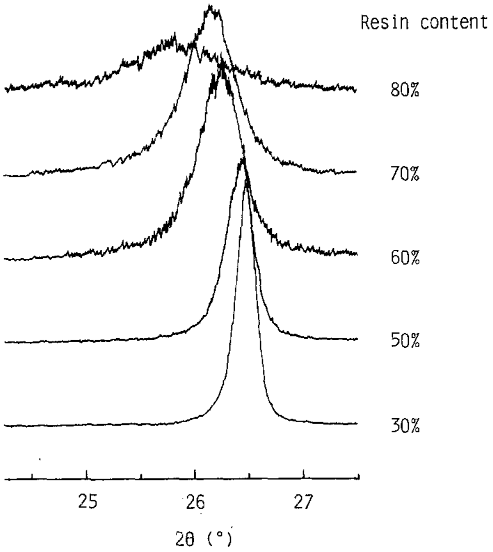

Figure 4 002 diffraction profiles of the 2800° C-treated carbons made from pitch/novolac-type resin mixtures by carbonization in a sealed gold tube under a pressure of 30 MPa.

These changes in structural parameters with resin content show good correspondence to the optical texture change shown in Figs. 1 and 2. It is known that the optical texture of carbonaceous materials definitely affects the structure and the graphitizability of the carbons [13–15]. From Figs. 2 and 5 some correspondence between optical texture and structural parameters can be seen; isotropic carbon gives $d_{002} > 0.342$ nm, L_c and L_a of < 10 nm; fine mosaic texture to $d_{002} = 0.337$ to 0.342 nm, $L_c = 10$ to 50 nm and $L_a = 10$ to 100 nm, medium and coarse mosaic texture gives $d_{002} < 0.337$ nm, $L_c < 50$ nm and $L_a < 100$ nm.

4. Conclusion

Of the factors influencing the properties of carbon/carbon composites, optical texture, graphitizability and yield of matrix carbon are important. The use of a pitch–phenolic resin system as a precursor for matrix carbon and the pressure of carbonization is advantageous in the preparation of carbon fibre/carbon composites. The fact that carbons with a wide range of optical texture and graphitizability can be prepared from a combination of precursors, pitch and phenolic resin, also suggests various possibilities of developing and improving the carbon products.

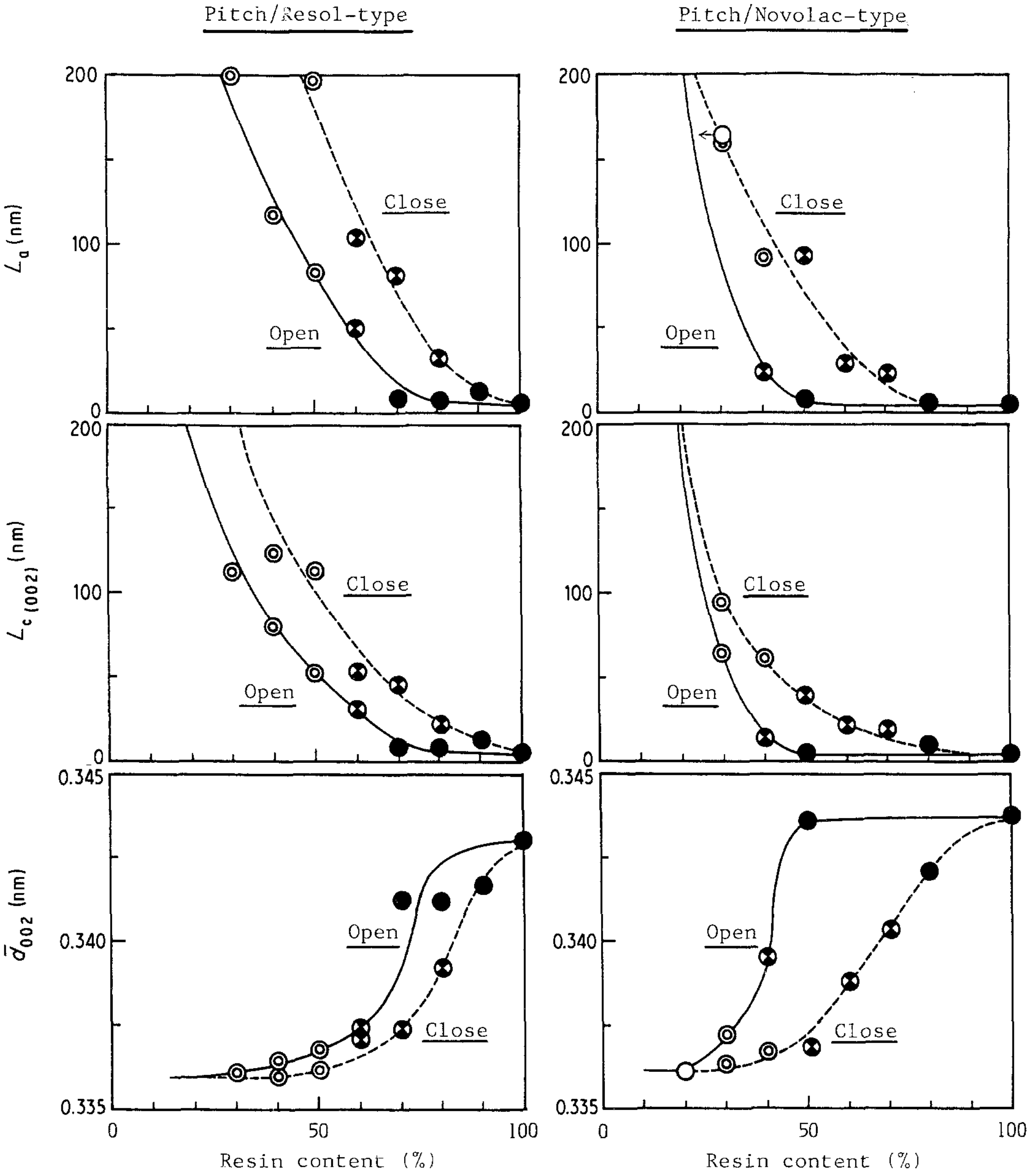

Figure 5 Changes in X-ray structural parameters of the 2800°C-treated carbons with resin content in the starting pitch/phenolic resin mixtures.

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